

# Reverse Micelle Based Synthesis of Microporous Materials in Microgravity

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## Introduction

Microporous materials include a large group of solids of varying chemical composition as well as porosity. These materials are characterized by channels and cavities of molecular dimensions. The framework structure is made up of interconnecting T-O-T' bonds, where T and T' can be Si, Al, P, Ga, Fe, Co, Zn, B and a host of other elements. Materials with Si-O-Al bonding in the framework are called zeolites and are extensively used in many applications. Ion-exchange properties of these materials are exploited in the consumer and environmental industries. Chemical and petroleum industries use zeolites as catalysts in hydrocarbon transformations. Synthesis of new microporous frameworks has led to the development of new technologies, and thus considerable effort worldwide is expended in their discovery. Microporous materials are typically made under hydrothermal conditions. Influence of nature of starting reactants, structure directing agents, pH, temperature, aging all have profound influence on the synthesis process. This is primarily because the most interesting open frameworks are not necessarily the stable structures in the reaction medium. Thus, the discovery of new frameworks is often tied to finding the right composition and synthesis conditions that allow for kinetic stabilization of the structure. This complexity of the synthesis process and limited understanding of it has made it difficult to develop directed synthesis of microporous materials and most advances in this field have been made by trial and error. The basic issues in crystal growth of these materials include

- Nature of the nucleation process
- Molecular structure and assembly of nuclei
- Growth of nuclei into crystals
- Morphology control
- Transformation of frameworks into other structures.

The NASA-funded research described in this paper focuses on all the above issues and has been described in several publications.<sup>1-6</sup> Below we present the highlights of our program, especially with the focus on possible experiments in microgravity.

## Results and Discussion

**a) Reverse Micelle Based Synthesis:** Our primary focus in developing this area of research has been to investigate if we can take advantage of the considerably lower rates of sedimentation in microgravity.

**Synthesis Process:** Conventional synthesis of microporous materials usually involves mixing together reactants in an aqueous medium and results in immediate formation of an amorphous precipitate, often referred to as the gel. Crystal growth proceeds from the gel. Several experiments have been reported using such procedures under microgravity conditions. Because of the presence of the gel, it is difficult to analyze the reaction process. Our approach has been to develop a new method of microporous materials synthesis that avoids the formation of the gel and makes the system more amenable to analysis during

crystal growth. The microporous materials that we focus on are zincophosphates, and we refer to them as ZnPO. Reverse micelles have been demonstrated over several decades to be an unique reaction medium for synthesis of nanoparticles of a wide class of materials. We were the first to report that microporous materials can also be synthesized under the appropriate conditions from reverse micellar reactants. The metastable nature of microporous materials requires a well-controlled compositional environment for synthesis and the particular reverse micelle needs to be chosen carefully. Thus, the open-pore framework zincophosphate X (ZnPO-X) with a faujasite structure could not be synthesized with AOT reverse micelles, because the high levels of  $\text{Na}^+$  in the water pool thwarted the nucleation of ZnPO-X and promoted the formation of a more condensed structure zincophosphate sodalite (ZnPO-S). Figure 1 compares these two frameworks. Understanding the reasons for failure of AOT reverse micelles in growing ZnPO-X led to the examination of cationic reverse micelles, especially the two-tailed surfactant dimethyldioctylammonium chloride (DODMAC), and its use resulted in the successful synthesis of ZnPO-X.

**Crystallization Pathways:** We have examined the nucleation and crystal growth process of ZnPO-X and ZnPO-S from reverse micelles in detail. The important step in formation of crystal nuclei involve exchange processes between reverse micelles, as depicted in Figure 2. If reactant composition is chosen such that only a small fraction of the micelles have the right supersaturation to form nuclei, then these nuclei can commence crystal growth using up the non-nucleated reverse micelles. After the crystals reach a certain size, they begin to settle via gravity, avoiding further growth in size. This process of crystal nucleation, growth and settling process can continue for days. On the other hand, if the reactant composition is such that supersaturation is exceeded in a large fraction of the micelles, then rapid precipitation of an amorphous solid can occur, resembling the conventional synthesis. This control over crystallization pathways by minor changes in the reactant composition is unique to the reverse micellar medium.

**Sedimentation Control:** The observation that crystal growth ceases on settling led us to examine ways to keep crystals suspended in the reaction medium. We have used rotation cells, which by gentle centrifugal forces can counteract gravity. Both ZnPO-S from AOT detergent system as well as ZnPO-X using DODMAC were examined. Unfortunately, aggregation of crystallites occurred, leading us to the conclusion that although the crystals could be suspended for longer periods of time in rotating cells, the experimental results were not meaningful.

Another approach we have developed for controlling crystal size is via a seeding process. We had observed that the yields of the ZnPO-X produced by the reverse micellar reaction were in the range of 15-20%, indicating that a significant fraction of zinc and phosphate species were still present in the organic medium. We rationalized the reason for the low yields on the basis of the micellar exchange process discussed earlier (Figure 2). As crystal growth occurs from nucleated reverse micelles, the composition of the non-nucleated reverse micelles also change with time via collisional exchange, and eventually more of these have the right composition to form nuclei. However, this leads to a decrease in non-nucleated reverse micelles that are the source for nutrients available for growth. Eventually the reverse micelles with nuclei have no source of remaining nutrients and the crystal growth stops. However, this solution with nuclei acts as an excellent seed system for growth of new crystals if provided with a source of reverse micelles as nutrients. The seed solution was added to a reverse micelle system that provided a source of nutrients, in narrow columns of varying lengths. Three such experiments were performed with columns of height of 0.71, 1.78 and 2.62 meters. Products were collected from the bottom of the column after one day

for the two shorter columns and after two days for the longer column. From the SEM images shown in Figure 3, we observed an average size of 3, 6 and 15  $\mu\text{m}$  with increasing column height, respectively. The size of the crystals was increased by controlling the time they spend in the medium, which depended on the length of the column.

**b) Morphological Control and Crystal Dissolution Pathways:** A second emphasis of our research program has been to develop experiments that take advantage of the decrease in buoyancy-driven convection in microgravity. This has focused on developing synthetic strategies to modify morphology and examine crystal transformation of different frameworks. Morphological control of microporous crystalline materials via synthetic routes is important for several reasons. For instance, it provides information about parameters that control nucleation and crystal growth, thereby illuminating aspects of the synthesis mechanism. Also, control of morphology is important for targeting various applications. We have shown that by altering composition, the morphology ZnPO-X could be changed. Previously reported synthesis of ZnPO-X at 4°C led to the formation of crystals with the characteristic octahedral morphology of faujasitic structures. Sizes of these crystals are in the  $<10\ \mu\text{m}$  range. We found that by increasing the TMAOH/H<sub>3</sub>PO<sub>4</sub> and Zn<sup>2+</sup>/Na<sup>+</sup> ratios, the morphology was drastically altered to produce large hexagonal platelet type crystals with diameters around 100  $\mu\text{m}$ . Figure 4 demonstrates the morphological change. Based on electron microscopy data, we concluded that the presence of twin planes was leading to crystals with the platelet-like morphology.

The possibility of synthesizing reasonably large flat crystals of ZnPO-X has made it feasible to do detailed Raman microprobe spectroscopic experiments. In particular, we have focused on microprobe Raman spectroscopy and examined how dissolution of ZnPO-X crystals occurs as a function of different monovalent cations in the medium. The vibrational information obtained from Raman spectroscopy made it possible to analyze the structural changes at the molecular level. In the presence of H<sup>+</sup>, at a pH of 3, the vibrational bands due to ZnPO-X disappeared completely in 12 minutes. These were replaced by Raman bands of hopeite, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, a condensed form of zincophosphate. Electron microscopic experiments showed that the ZnPO-X was gradually getting covered with a film of hopeite. If, instead of H<sup>+</sup>, Li<sup>+</sup>, or Cs<sup>+</sup> were used, then the ZnPO-X gradually converted to framework structures of LiA(BW) and CsZnPO<sub>4</sub>, respectively. How H<sup>+</sup>, Li<sup>+</sup> and Cs<sup>+</sup> destabilize in the ZnPO-X structure was also manifested in the vibrational band of tetramethylammonium (TMA) ions trapped in the sodalite cages of ZnPO-X. Upon exchange with H<sup>+</sup>, Li<sup>+</sup>, and Cs<sup>+</sup>, prior to collapse of the ZnPO-X and loss of TMA from the Raman spectra, there is a significant broadening of the TMA band at 765 cm<sup>-1</sup>. The bandwidth changes from  $\sim 6\ \text{cm}^{-1}$  for Na<sup>+</sup> to 11, 12 and 16 cm<sup>-1</sup> for H<sup>+</sup>, Cs<sup>+</sup> and Li<sup>+</sup>, respectively. Our interpretation is that, upon ion-exchange with these cations, there is a distortion of the ZnPO-X framework, which makes the framework more susceptible to hydrolysis.

**Influence of Framework Topology on Crystal Dissolution:** Our primary interest is a fundamental understanding of the molecular assembly of microporous materials. Can that goal be attained by examining crystal dissolution? We believe that to be the case for several reasons. First, the most interesting microporous frameworks are metastable structures and evolve to more condensed topologies with time. Second, clues regarding the complexity of the dissolution fragments of different frameworks provide information about the stability of the building units.

In addition to Raman spectroscopy, we are developing several other techniques using to study the crystal dissolution process. The UV-Visible spectroscopic technique involves use a pH sensitive dye. The dissolution of sodalite and ZnPO-X at low pH and the deposition of

hopeite changes the Zn/P ratio, thus releasing the phosphate ions in solution which increases the pH of solution close to the surface. We have monitored this pH change with a colorimetric dye. Figure 5 shows the change in UV-visible spectra around a dissolving ZnPO-S crystal with time. We are planning to extend this study to use fluorescence microprobe techniques for better spatially sensitive measurements. These studies are providing us useful data for developing mathematical models of the crystal dissolution process. Influence of buoyancy-driven convection on the dissolution process is expected to be different for frameworks of different topologies.

**c) Proposed experiments in Microgravity:** There are two aspects of microgravity that we want to exploit. These include lack of sedimentation and absence of buoyancy driven convection. As we have demonstrated, under particular conditions of reverse micelle composition, crystal growth occurs in a layer-by-layer fashion. Avoiding sedimentation in these systems will lead to the growth of larger crystals. Light scattering will be used to follow the growth of crystals in microgravity. Seeding experiments to grow larger crystals is also possible, something that has not been accomplished in conventional synthesis.

The second aspect of the microgravity experiments will focus on microprobe Raman studies, and absorption/fluorescence microscopy based on pH sensitive dyes. By comparing results in 1g and microgravity, we will discover if different surface intermediates are present during dissolution of different frameworks.

## References

1. Crystal Growth of Faujasitic Microporous Zincophosphate Crystals Using Reverse Micelles as Reactants. Ramsharan Singh and Prabir K. Dutta, *Langmuir* **2000**, *16*, 4148-4153.
2. Synthesis of microporous faujasitic-like zincophosphates from reverse micelles, Mario J. Castagnola and Prabir K. Dutta, *Microporous and Mesoporous Materials* **2000**, *34*, 61-65.
3. Crystal growth of zincophosphates from conventional media and reverse micelles: mechanistic implications. Mario J. Castagnola and Prabir K. Dutta, *Microporous Mesoporous Mater.* **1998**, *20*, 149-159.
4. Reverse Micelle Based Growth of Zincophosphate Sodalite: Examination of Crystal Growth. K. S. N Reddy, L. M. Salvati, Prabir K. Dutta, Phillip B. Abel, Kwang I. Suh and Rafat R. Ansari, *J. Phys. Chem.* **1996**, *100*, 9870-9880.
5. Controlled growth of microporous crystals nucleated in reverse micelles. Prabir K. Dutta, Michael Jakupca, K. Satya Narayana Reddy and Louis Salvati, *Nature (London)* **1995**, *374*, 44-6.
6. Synthesis of Platelet-Like Faujasitic Zincophosphate X Crystals, M. J. Castagnola, P. K. Dutta, Proceedings of the 12<sup>th</sup> International Zeolite Conference, Materials Research Society, **1999**, 1627-1632.

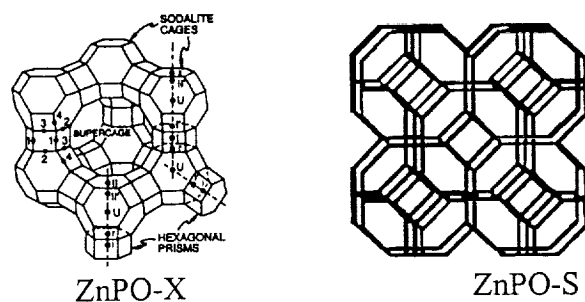


Figure 1. Microporous frameworks of interest to this study.

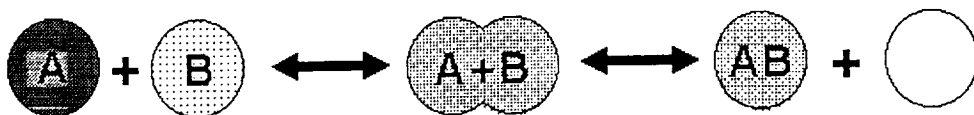


Figure 2. Exchange processes in reverse micelles.

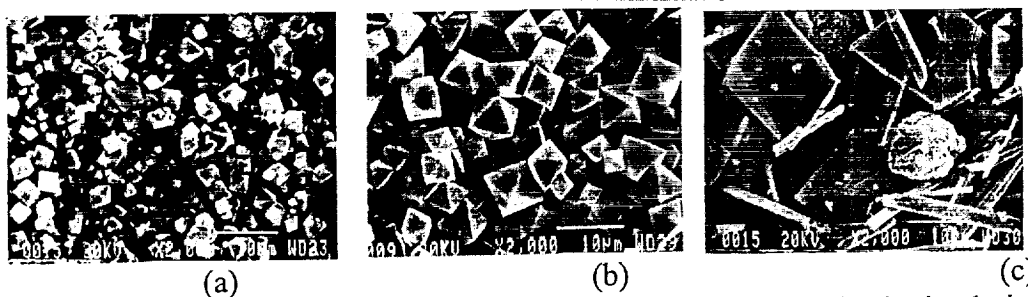


Figure 3. The scanning electron micrograph of ZnPO-X crystals obtained via the reverse micelle experiment from columns of various length, (a) after 1 day from a height of 0.71 meter reaction mixture, (b) after 1 day from a height of 1.78 meter reaction mixture and (c) after 2 days from a height of 2.62 meter reaction mixture.



Figure 4. Scanning electron micrograph of ZnPO-X dissolving crystals obtained via control of composition.

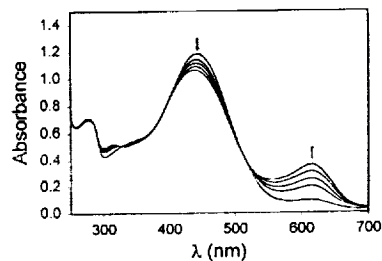


Figure 5. pH change around a ZnPO-S crystal with time as measured by the spectrum of dye.